

药用植物盆架树中的缩醛*

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摘要: 夹竹桃科药用植物盆架树 (*Winchia calophylla*) 茎皮的乙醇提取物, 经石油醚脱脂后用盐酸和氨水处理, 再用石油醚、氯仿和正丁醇萃取。从正丁醇部分分离出 6 个化合物, 其中 3 个为新成分, 分别命名为盆架丁基缩醛、异盆架丁基缩醛和盆架乙基缩醛; 另 3 个已知化合物依次为丁基- β -D-呋喃葡萄糖甙、丁基- β -D-吡喃葡萄糖甙和丁基- α -D-吡喃葡萄糖甙。他们可能是人工产物。

关键词: 盆架树; 夹竹桃科; 丁基糖甙; 缩醛

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Butyl Acetals from Medicinal Plant, *Winchia calophylla* (Apocynaceae) *

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Abstract: Three new compounds, butyl winchal, butyl isowinchal and ethyl winchal along with three known compounds, butyl β -D-glucofuranoside, butyl β -D-glucopyranoside and butyl α -D-glucopyranoside, were isolated from the stem barks of *Winchia calophylla* dealt with hydrochloric acid and aqueous ammonia. Their structures were established by spectroscopic methods, especially 2D NMR data. They are probably artificial products.

Key words: *Winchia calophylla*; Apocynaceae; Butyl glycoside; Winachal

Winchia calophylla A. DC. (Apocynaceae), distributed in Yunnan and Hainan Provinces of China, India, Myanmar and Indonesia, is a traditional Dai medicinal plant (Delectis Florae Reipublicae Popularis Sinicae Agendae Academiae Sinicae, 1977).

Results and discussion

Previously, we reported the isolations and identifications of triterpenoids (Zhu *et al.* 2001), monoter-

pene cyclo-diglycosides (Zhu *et al.* 2003; 2004a), iridoid glycosides (Zhu *et al.* 2004b), and indole alkaloids (Zhu *et al.* 2005) from this plants. Continuous studies led to the isolation and elucidation of three new compounds, butyl winchal (1), butyl isowinchal (2) and ethyl winchal (3), together with three known compounds, butyl β -D-glucofuranoside (4) (Straathof *et al.* 1987), butyl β -D-glucopyranoside (5) (Usui *et al.* 1973), butyl α -D-glucopyranoside (6) (Fabre *et*

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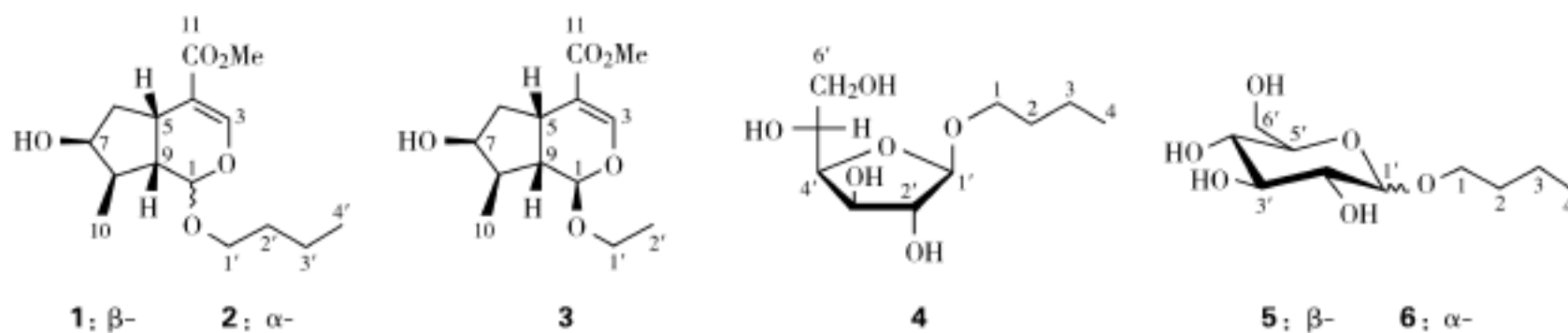


Fig. 1 The structures of compounds 1-6

al. 1993). Their structures were determined by spectroscopic analysis, especially 2D NMR experiments.

The high resolution EIMS showed both **1** and **2** possess the same molecular formula $C_{15}H_{24}O_5$ at m/z 284.1615 and 284.1613 (calcd. 284.1624), respectively. EIMS of **1** gave the fragment ion peaks at m/z 266 ($M^+ - 18$), 253 ($M^+ - 31$) and 210 ($M^+ - 74$), which indicated the presence of -OH, MeO- and BuO- in the framework. ^1H NMR spectra showed the molecule bearing a vinyl proton (δ 7.38, d, 1H, $J = 1.0$ Hz), acetal proton (δ 4.71, d, 1H, $J = 5.0$ Hz), oxymethine (δ 4.02, br. t, 1H, $J = 4.6$ Hz), oxymethylene (δ 3.55, dt, 1H, $J = 6.5, 9.6$ Hz and 3.83, dt, 1H, $J = 6.5, 9.6$ Hz), methoxyl (δ 3.68, s, 3H), secondary methyl (δ 1.08, d, 3H, $J = 7.0$ Hz) and preliminary methyl (δ 0.92, t, 3H, $J = 7.4$ Hz). The ^{13}C NMR (DEPT) spectra showed 15 signals including a -COO-, $C = CH$, OCHO, OCH, OCH_2 , OCH_3 , three CH, three CH_2 and two CH_3 , which were very similar to those of loganin (Zhu *et al.* 2004b), except for the added signals of *n*-butoxyl and the absence of signals of β -D-glucopyranosyl residue, indicating that **1** was a iridoid. By comparing with those of loganin, the shift effects $\Delta\delta + 4.7$ and -0.56 were observed for C - 1 and H - 1, respectively. HMBC spectra showed the ^1H - ^{13}C long-range correlations between H - 1 (δ 4.71, d, 1H, $J = 5.0$ Hz)

with C - 1' (δ 70.2), and H - 1' (δ 3.55, dt, 1H, $J = 6.5, 9.6$ Hz and 3.83, dt, 1H, $J = 6.5, 9.6$ Hz) with C - 1 (δ 102.5) (Fig. 2). The Key NOE correlations between H - 5 with H - 9, H - 7 with H - 8, H - 1 with H - 8, and H - 9 with H - 10 were observed in the NOESY experiment (Fig. 2). Thus, the structure of compound **1** was elucidated to be methyl 1 β -*n*-butoxy-7 β -hydroxy-8 β -methyl-2-oxa-bicyclo[4.3.0]-5 β , 9 β -nona-3-en-4-carboxylate.

The EIMS, ^1H and ^{13}C NMR spectra of compound **2** were quite similar to those of **1**, except for the downfield shift of H - 1 (+ 0.33 ppm) and C - 8 (+ 2.6 ppm), the highfield shift of C - 10 (- 1.4 ppm), and the diminution of $J_{1,9}$ from 5.0 to 3.3 Hz, indicating that **2** was the epimer of **1** at C - 1 (Fig. 2). When the stereochemistry of 1-butoxyl substitution changed from β to α -form, the butoxyl group would shield C - 8 and deshield C - 10, which resulted C - 8 downfield shifted and C - 10 highfield shifted. Thus, the structure of compound **2** was determined to be methyl 1 α -*n*-butoxy-7 β -hydroxy-8 β -methyl-2-oxa-bicyclo[4.3.0]-5 β , 9 β -nona-3-en-4-carboxylate.

The high resolution EIMS of compound **3** showed the molecular ion peak at m/z 256.1298 corresponding to the molecular formula $C_{13}H_{20}O_5$ (calcd. 256.1311). EIMS gave the fragments at m/z 238 ($M^+ - 18$), 225 ($M^+ - 31$) and 210 ($M^+ - 46$) corresponding to the cleav-

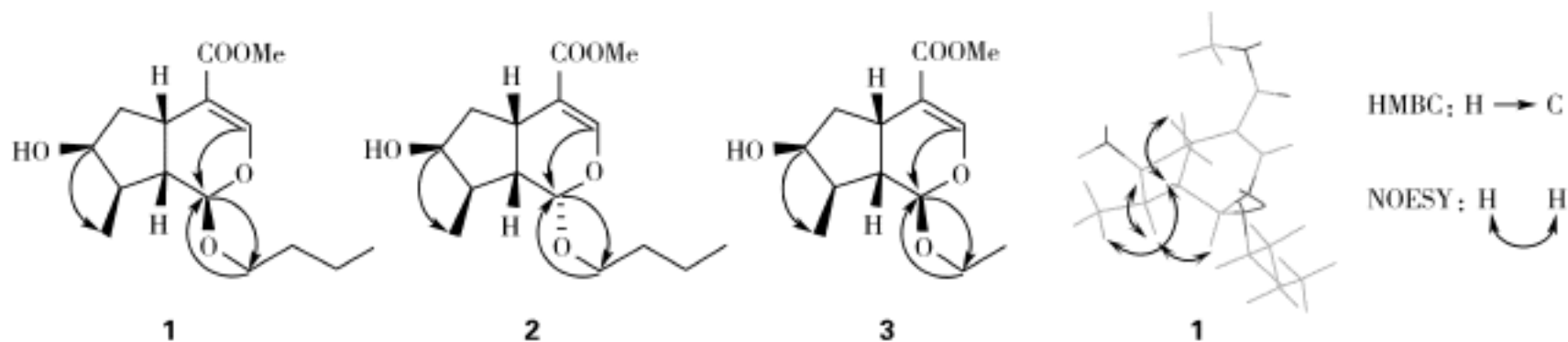


Fig. 2 The selected HMBC correlations of 1-4 and key NOESY correlations of 1

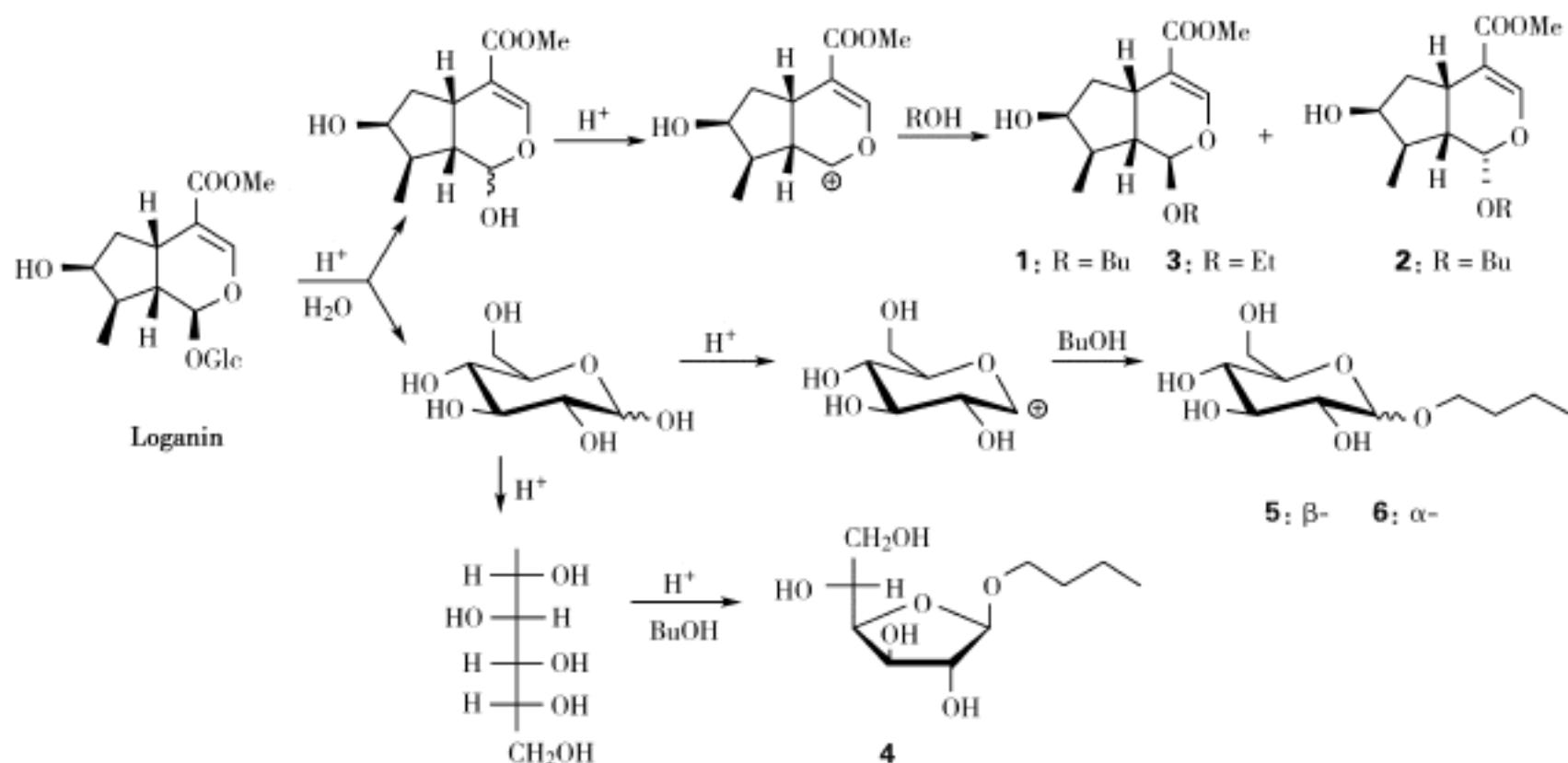


Fig. 3 The probable formation pathway of 1 - 6

age of HO-, MeO- and EtO-. The ^1H and ^{13}C NMR spectra were very similar to those of **1** except for the lack of signals of four protons and two methylene carbons in the high field, indicating that butyl in **1** was substituted by ethyl in **3**, which was further confirmed by HMBC experiment (Fig. 2). Thus, the structure of compound **3** was determined to be methyl 1 β -*n*-ethoxy-7 β -hydroxy-8 β -methyl-2-oxabicyclo [4.3.0]-5 β , 9 β -nona-3-en-4-carboxylate.

These compounds probably resulted from loganin and glucose by corresponding alcoholysis in the acidic condition of extractions (Fig. 3).

Experimental

General Experimental Procedures Optical rotations were determined on a JASCO-20 polarimeter. IR spectra were obtained on KBr pellets using a Bio-Rad FTS-135 spectrometer. The ^1H and ^{13}C NMR spectra were recorded on BRUKER AM-400 and/or DRX-500 with TMS as internal standard. The chemical shifts are reported in δ units (ppm). EIMS and HRFABMS measurements were carried out on a VG Auto Spec-3000 spectrometer. TLC and column chromatography were performed on plates precoated with silica gel F₂₅₄ and over silica gel H (Qingdao Marine Chemical Ltd., China), respectively. Solvents were distilled prior to use.

Plant Material The stem barks of *W. calophylla* were collected in Xishuangbanna, Yunnan Province of China, in the July 2000 and were identified by Prof. Liu Hong Mao and Mr. Cui Jing Yun. The voucher specimen was deposited in the

Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences.

Extraction and Isolation The dried and ground stem barks (10.5 kg) of *W. calophylla* were extracted four times with 95% EtOH under reflux. Removal of the solvents in vacuum produced a concentrated syrupy (600 g) which was partitioned between petroleum ether and water. The petrol.-insoluble fraction was dissolved in 2% HCl (4 × 500 ml). The acidic solution was adjusted to pH 9-10 with concentrated ammonia and the obtained basic solution was then extracted with petroleum ether (3 × 600 ml), chloroform (3 × 600 ml), *n*-butanol (3 × 500 ml) in turns.

The butanol fraction (180 g) was subjected to flash column chromatography over silica gel H eluting with ethyl acetate and gradient EtOAc-MeOH to afford seven fractions, BO-1 ~ BO-7. The fraction BO-2 (~16 g) was separated into two parts, BO-21 and BO-22, by gel chromatography (LH-20) eluting with MeOH. The residues BO-21 (~2 g) rechromatographed over silica gel H eluting with 30:2:1 petroleum ether-acetone-diethylamine to afford compound **3** (16 mg). The fraction BO-3 (9 g) was again separated into three parts, BO-31, BO-32 and BO-33 by flash column chromatography over silica gel H (30:1 EtOAc-MeOH). The residues BO-31 (~2 g) rechromatographed over reverse-phase silica gel (RP-18) eluting with 3:2 MeOH-H₂O to give compounds **5** (410 mg) and **6** (12 mg). The fraction BO-32 (~2 g) gave compound **4** (362 mg) through repeated flash column chromatography over silica gel H eluting with CHCl₃-MeOH (30:1). The residues BO-4 (~5 g) was subjected to repeated chromatography over silica gel H and reverse-silica gel (RP-18)

to afford compound **1** (37 mg) and **2** (12 mg) .

Butyl winchal (**1**) was obtained as oil . $[\alpha]_{\text{D}}^{26}$ - 66.8 (*c* 1.40, MeOH) . EIMS m/z (%): 284 (M^+ , 82), 266 (77), 253 (37), 234 (30), 222 (25), 210 (88), 192 (48), 178 (90), 160 (39), 139 (70), 128 (96), 109 (32), 97 (51), 83 (35), 71 (42), 57 (100) . ^1H NMR (500 MHz, d_4 -MeOH) δ : 4.71 (d, $J=5.0$ Hz, 1H, H-1), 7.38 (d, $J=1.0$ Hz, 1H, H-3), 3.06 (ddd, $J=8.2$ Hz, 1H, H-5), 1.50-1.53 (m, 1H, H-6a), 1.75-1.78 (m, 1H, H-6b), 4.02 (br.t, $J=4.6$ Hz, 1H, H-7), 1.90 (t, $J=5.0$ Hz, 1H, H-8), 2.23 (ddd, $J=4.5, 9.0, 9.0$ Hz, 1H, H-9), 1.08 (d, $J=7.0$ Hz, 3H, H-10), 3.68 (s, 3H, $-\text{OCH}_3$), 3.55 (dt, $J=6.5, 9.6$ Hz, 1H, H-1'a), 3.83 (dt, $J=6.5, 9.6$ Hz, 1H, H-1'b), 1.55 (q, $J=7.4$ Hz, 2H, H-2'), 1.39 (q, $J=7.4$ Hz, 2H, H-3'), 0.92 (t, $J=7.4$ Hz, 3H, H-4') . ^{13}C NMR (125 MHz, d_4 -MeOH) δ : 102.1 (d, C-1), 152.8 (d, C-3), 113.4 (s, C-4), 33.5 (d, C-5), 42.2 (t, C-6), 75.4 (d, C-7), 40.0 (d, C-8), 47.5 (d, C-9), 15.0 (q, C-10), 169.6 (s, C-11), 70.2 (t, C-1'), 32.8 (t, C-2'), 20.4 (t, C-3'), 14.0 (q, C-4'), 51.6 (q, MeO-) .

Butyl isowinchal (**2**) was obtained as oil . $[\alpha]_{\text{D}}^{26}$ + 85.7 (*c* 0.75, MeOH) . EIMS m/z (%): 284 (M^+ , 42), 266 (34), 253 (17), 234 (11), 222 (9), 210 (41), 192 (16), 178 (37), 160 (10), 139 (35), 127 (91), 109 (22), 97 (29), 81 (27), 71 (100), 57 (76) . ^1H NMR (500 MHz, d_4 -MeOH) δ : 5.04 (d, $J=3.3$ Hz, 1H, H-1), 7.39 (t, $J=1.3, 2.0$ Hz, 1H, H-3), 3.04 (q, $J=7.8$ Hz, 1H, H-5), 1.66-1.70 (m, 1H, H-6a), 2.04-2.11 (m, 2H, H-6b and H-8), 4.06-4.10 (m, 1H, H-7), 2.21 (q, $J=7.5$ Hz, 1H, H-9), 1.09 (d, $J=7.2$ Hz, 3H, H-10), 3.68 (s, 3H, $-\text{OCH}_3$), 3.48 (dt, $J=6.5, 9.6$ Hz, 1H, H-1'a), 3.79 (dt, $J=6.5, 9.6$ Hz, 1H, H-1'b), 1.54 (q, $J=7.5$ Hz, 2H, H-2'), 1.38 (q, $J=7.5$ Hz, 2H, H-3'), 0.92 (t, $J=7.5$ Hz, 3H, H-4') . ^{13}C NMR (125 MHz, d_4 -MeOH) δ : 102.5 (d, C-1), 152.5 (d, C-3), 113.4 (s, C-4), 32.6 (d, C-5), 42.9 (t, C-6), 75.0 (d, C-7), 42.6 (d, C-8), 46.5 (d, C-9), 13.6 (q, C-10), 169.6 (s, C-11), 70.2 (t, C-1'), 32.8 (t, C-2'), 20.3 (t, C-3'), 14.6 (q, C-4'), 51.6 (q, MeO) .

Ethyl winchal (**3**) was obtained as oil . $[\alpha]_{\text{D}}^{26}$ - 33.4 (*c* 0.95, MeOH) . EIMS m/z (%): 256 (M^+ , 20), 238 (19), 225 (15), 210 (21), 192 (14), 178 (20), 160 (14), 139 (20), 126 (21), 111 (19), 99 (100), 81 (22), 71 (62) . ^1H NMR (500 MHz, d_4 -MeOH) δ : 4.74 (d, $J=4.8$ Hz, 1H, H-1), 7.67 (d, $J=1.0$ Hz, 1H, H-3), 3.61 (dd, $J=7.1, 9.8$ Hz, 1H, H-5), 1.77-1.82 (m, $J=4.8, 13.6$ Hz, 1H, H-6a), 2.22 (ddd, $J=1.3, 8.0, 13.6$ Hz, 1H, H-6b),

4.02 (br.t, $J=4.6$ Hz, 1H, H-7), 1.52-1.56 (m, $J=4.9, 7.0, 8.0$ Hz, 1H, H-8), 1.91 (ddd, $J=4.8, 9.0, 9.0$ Hz, 1H, H-9), 1.00 (d, $J=6.9$ Hz, 3H, H-10), 3.68 (s, 3H, $-\text{OCH}_3$), 3.04 (q, $J=7.1$ Hz, 1H, H-1'a), 3.86 (q, $J=7.1$ Hz, 1H, H-1'b), 1.12 (t, $J=7.1$ Hz, 3H, H-2') . ^{13}C NMR (125 MHz, d_4 -MeOH) δ : 102.2 (d, C-1), 152.5 (d, C-3), 113.5 (s, C-4), 32.5 (d, C-5), 42.9 (t, C-6), 75.2 (d, C-7), 42.5 (d, C-8), 46.9 (d, C-9), 13.6 (q, C-10), 169.6 (s, C-11), 65.9 (t, C-1'), 15.4 (q, C-2'), 51.6 (q, MeO-) .

Butyl β -D-glucofuranoside (**4**) was obtained as oil . $[\alpha]_{\text{D}}^{14}$ - 78.0 (*c* 2.60, MeOH) . EIMS m/z (%): 237 (M^+ + 1, 8), 236 (M^+ , 6), 205 (5), 187 (4), 175 (89), 163 (90), 158 (50), 145 (38), 129 (51), 116 (77), 101 (92), 91 (85), 86 (89), 69 (95), 55 (100) . ^1H NMR (500 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 3.47 (dd, $J=6.7, 15.5$ Hz, 1H, H-1a), 3.89 (dd, $J=7.0, 15.5$ Hz, 1H, H-1b), 1.48-1.54 (m, $J=6.7, 7.0, 7.3$ Hz, 2H, H-2), 1.26-1.33 (m, $J=7.3$ Hz, 2H, H-3), 0.77 (t, $J=7.3$ Hz, 3H, H-4), 5.42-5.45 (m, 1H, H-1'), 4.78-4.82 (m, 2H, H-2' and H-5'), 4.89-4.93 (m, 2H, H-3' and H-4'), 4.32 (dd, $J=6.8, 11.0$ Hz, 1H, H-6'a), 4.47 (dd, $J=3.5, 11.0$ Hz, 1H, H-6'b) . ^{13}C NMR (125 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 68.2 (t, C-1), 32.7 (t, C-2), 19.7 (t, C-3), 14.0 (q, C-4), 110.1 (d, C-1'), 82.2 (d, C-2'), 78.0 (d, C-3'), 82.7 (d, C-4'), 72.2 (d, C-5'), 65.6 (t, C-6') .

Butyl β -D-glucopyranoside (**5**) was obtained as oil . $[\alpha]_{\text{D}}^{14}$ - 13.9 (*c* 0.485, MeOH) . EIMS m/z (%): 237 (M^+ + 1, 22), 205 (22), 187 (19), 163 (66), 144 (68), 131 (22), 116 (100), 103 (29), 98 (62), 85 (65), 69 (48), 56 (45) . ^1H NMR (400 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 4.05 (ddd, $J=2.6, 6.8, 15.2$ Hz, 1H, H-1a), 3.61 (ddd, $J=2.5, 7.8, 15.2$ Hz, 1H, H-1b), 1.53-1.59 (m, $J=6.8, 7.5, 7.8$ Hz, 2H, H-2), 1.28-1.33 (m, $J=7.4, 7.5$ Hz, 2H, H-3), 0.76 (t, $J=7.4$ Hz, 3H, H-4), 4.76 (d, $J=7.8$ Hz, 1H, H-1'), 4.15 (t, $J=7.8, 8.9$ Hz, 1H, H-2'), 4.21 (t, $J=8.9$ Hz, 1H, H-3'), 3.97 (t, $J=8.9$ Hz, 1H, H-4'), 3.89-3.91 (m, $J=2.5, 5.8$ Hz, 1H, H-5'), 4.50 (dd, $J=2.0, 11.8$ Hz, 1H, H-6'a), 4.32 (dd, $J=5.8, 11.8$, 1H, H-6'b) . ^{13}C NMR (100 MHz, $\text{C}_5\text{D}_5\text{N}$) δ : 69.8 (t, C-1), 32.5 (t, C-2), 19.8 (t, C-3), 14.3 (q, C-4), 104.8 (d, C-1'), 75.3 (d, C-2'), 78.5 (d, C-3'), 71.9 (d, C-4'), 78.7 (d, C-5'), 63.0 (t, C-6') .

Butyl α -D-glucopyranoside (**6**), was obtained as oil . $[\alpha]_{\text{D}}^{14}$ + 63.4 (*c* 0.359, MeOH) . EIMS m/z (%): 237 (M^+ + 1, 20), 205 (25), 187 (16), 163 (69), 144 (63), 131 (28), 116 (100), 103 (31), 98 (60), 85 (70), 69 (45), 56 (41) .

¹H NMR (400 MHz, C₅D₅N) δ: 4.03 - 4.07 (m, *J* = 6.5, 15.5 Hz, 1H, H-1a), 3.38 (dd, *J* = 6.5, 15.5 Hz, 1H, H-1b), 1.75 - 1.77 (m, *J* = 6.5, 7.2 Hz, 2H, H-2), 1.52 - 1.55 (m, *J* = 6.5, 7.2 Hz, 2H, H-3), 1.02 (t, *J* = 7.2 Hz, 3H, H-4), 5.19 (d, *J* = 3.4 Hz, 1H, H-1'), 4.83 (br.s, 1H, H-2'), 5.13 (t, *J* = 4.8, 9.6 Hz, 1H, H-3'), 3.65 - 3.68 (m, *J* = 9.1 Hz, 1H, H-4'), 3.61 - 3.64 (m, *J* = 6.1, 9.3 Hz, 1H, H-5'), 4.47 (br. d, *J* = 18.0 Hz, 1H, H-6'a), 4.31 (br. d, *J* = 18.0 Hz, 1H, H-6'b). ¹³C NMR (100 MHz, C₅D₅N) δ: 68.2 (t, C-1), 32.7 (t, C-2), 19.8 (t, C-3), 14.3 (q, C-4), 101.3 (d, C-1'), 75.1 (d, C-2'), 76.8 (d, C-3'), 70.2 (d, C-4'), 76.8 (d, C-5'), 62.8 (t, C-6').

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